

LIQUID FUELS FROM TARS BY CARBONIZATION OF COALS IN HYDROGEN ATMOSPHERES

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The purpose of this investigation was to determine the feasibility of producing a gasoline boiling range product of satisfactory yield and quality by low-temperature (950° F) carbonization of coal in hydrogen atmospheres below 1,000 psig, with immediate catalytic hydrotreating of tar vapors and liquid tar issuing from the coal. Information on the effects of varying hydrogen pressure and catalyst temperature on the yields of individual compounds of interest in the gasoline boiling range product was also desired.

Very little previous work has been done along these particular lines. With respect to the processing of the uncondensed tar vapors, Flinn and Sachs (1) conducted a low-temperature carbonization of a high-volatile bituminous coal at 445 psig hydrogen, passing the tar vapors through a cobalt-molybdenum on alumina catalyst at 800° F, obtaining in the vicinity of 100 lbs gasoline boiling range (up to 200° C) product per ton of coal. No information of any kind was reported on the individual constituents in this product.

With regard to the use of hydrogen pressures below 1,000 psig there is little information beyond that of Flinn and Sachs. Qader, *et al* (2) have reported hydrotreating of previously condensed tar over a cobalt-molybdenum catalyst at 420° C and pressures as low as 1,500 psig. This tar was produced from a mixture of high volatile A bituminous coal and 15 wt-pct stannous chloride at 2,000 psig hydrogen and 515° C. With these two steps the yield of gasoline was 26 wt-pct of the tar. Without the catalyst the yield of tar was 20 wt-pct, and although this tar was not hydrotreated, if one assumes comparable results as with the tar from the coal-catalyst mixture, the yield of gasoline would have been about 100 lbs per ton of coal. No information of any kind was given on individual compounds in the gasoline.

EXPERIMENTAL

The experimental equipment is shown schematically in Figure 1. The reactor was a stainless-steel vessel 5-7/8-in. ID and 20-in. in depth, designed for operation at 1,000° F and 1,000 psig. The reactor was heated electrically with external strip heaters, the temperature being measured and controlled by a chromel-alumel thermocouple placed at the inside reactor wall.

Coal charge and catalyst were contained in wire-mesh baskets inserted into the reactor, the catalyst basket being at the bottom. Temperature of the coal bed was measured with a chromel-alumel thermocouple inserted in the bed center. Channeling of the gas stream around the thermowell, due to variable packing, settling, and shrinkage of the coal bed, led to variations in the recorded coal bed temperatures from the usual reactor temperature of about 950° F. The catalyst,

when in this same reactor, was probably in the vicinity of 950° F. This arrangement was used in the first 12 runs. For the last 9 runs a separate catalyst holder was installed, external to the carbonizing reactor, and with its own electrical heater to permit operating the catalyst bed at temperatures different from the reactor proper. The catalyst bed temperature was measured by a chromel-alumel thermocouple inserted into the bed. In these runs the coal bed had an annular configuration, as shown in Figure 1. The coal and catalyst bed temperatures for the 21 runs are shown in Table 1.

In operation, hydrogen, metered through an orifice meter at 8 to 10 SCFH (300 to 900 psig), was passed downward through coal and catalyst. Tar evolved during carbonization, both liquid and vapor, thus was carried down over the catalyst into an air cooled receiver, where heavier constituents were collected. Effluent vapors passed into a water-cooled condenser for further liquid collection, then through a regulating valve which controlled the system at desired operating pressure. Gases then passed into a silica gel trap to absorb uncondensed vapors and were metered through a wet test meter.

Coal used was Pittsburgh-seam high-volatile A bituminous, 40 to 60 mesh. The hydrodesulfurization catalyst was Girdler G-35B, a cobalt-molybdena on alumina in the form of 1/8-in. pellets. Analyses of the coal and char were made using standard ASTM methods.

Total liquid product was obtained by combining the contents of the air-cooled and water-cooled receivers. Any vapors trapped in the silica gel were counted as product but were not recovered. The liquid was distilled on a small glass Vigreux column taking an overhead weight of water and light oils (b. p. < 200° C) and discarding the water. A second distillation cut was made between 200° - 400° C and designated heavy oils. Any liquid product boiling above 400° C was reported as distillation residue. The light oils were analyzed by gas-liquid chromatography with the results shown in Table 2.

Gas samples were taken at intervals from the line before the wet-test meter. These were analyzed by gas-solid chromatography.

RESULTS AND DISCUSSION

As shown in Table 1, the lowest total oil yield, 56 lbs, was obtained when nitrogen was substituted for hydrogen in the runs with the catalyst. In the absence of the catalyst, as the hydrogen pressure increased from 300 to 600 to 900 psig the yield of total oil progressively decreased from 190 to 110 lbs.

The majority of the runs were made with 10 wt-pct catalyst, based on the coal. The yields of total oils and light oils produced from the tar vapors and liquid tar passing through this catalyst are shown in pounds per ton of dry ash-free coal versus hydrogen pressures from 0 to 900 psig at catalyst temperatures of 650°, 750°, and 950° F in Figures 2, 3, and 4, respectively. At all temperatures the yield of total oils declined with increasing pressure to a value of about 150 lbs, with increased formation of gas and water. However, the light oils, or material boiling up to 200° C, in these total oils increased, most dramatically at 750° F, rising from 10 lbs at 0 psig (1 atm hydrogen) to a maximum of about 100 lbs around 600 psig, or a ten-fold increase. The 650° runs also showed a maximum light oil yield at 600 psig.

The quality of this gasoline boiling range light oil at maximum yields was good. It was a completely clear, water-white liquid with a sweet, clean odor. Analyses demonstrated that it was olefin-free, and, as shown later, rich in BTX, that is, about 70 wt-pct benzene, toluene, and xylenes. The gas was likewise olefin-free and rich in methane, about 50 volume-pct. The presence of ammonia and hydrogen sulfide in obviously much larger amounts than experienced during ordinary low-temperature carbonizations of the same coal indicated that substantial denitrogenation and desulfurization occurred. Elemental analyses demonstrated that there were little or no nitrogen and sulfur compounds in the light oils obtained under the better operating conditions, as shown in Table 3. The oxygen values were determined by difference, and found to fluctuate around zero for those light oils with low nitrogen and sulfur contents.

From Figures 2, 3, and 4 it is evident that the operating conditions for maximum yield of gasoline boiling range product were a catalyst temperature of 750° F and a hydrogen pressure of 600 psig. Based on many studies, the recommended temperature at low hydrogen pressures for cobalt-molybdenum on alumina catalysts is in the vicinity of 750° F. At much higher temperatures, substantial cracking to gas is experienced. The impossibility of obtaining good light oil yields at temperatures as high as 950° F was demonstrated by the fact that at 900 psig hydrogen the same yield, 40 lbs, was obtained with no catalyst, with 10 wt-pct catalyst; and with 25 wt-pct catalyst.

The yields of desired individual compounds, in particular benzene and toluene, were as high, or higher, at 600 psig than at 900 psig, demonstrating that hydrogen pressures well below 1000 psig were practical. Figure 5 shows that the yields of benzene and toluene at 750° F rose from 1.4 and 3.6 lbs, respectively, at 0 psig to a maximum of about 29 lbs each at 600 psig. The yields of benzene and toluene at 0 psig were close to the yields typical in ordinary low-temperature carbonization of this same Pittsburgh-seam coal, with no treatment of the evolved tars (3, 4).

Figures 6 and 7 show the variations at 300 and 900 psig, respectively, in the yields of benzene, toluene, total xylenes, and total aliphatics in the light oils obtained at the various catalyst bed temperatures from 650° to 950° F. The curves for benzene are similar at these pressures up to 750° F, showing yields of about 13 lbs at this temperature. However, the 300 psig curve for benzene has its maximum at 750° F whereas the 900 psig curve rises a little to about 15 lbs at 950° F. The 750° F maximum for toluene is increased from about 19 lbs at 300 psig to about 25 lbs at 900 psig. As previously noted, the 750° F maximum for both benzene and toluene is about 29 lbs each at the intermediate pressure of 600 psig, which is the optimum pressure.

The xylenes curves in Figures 6 and 7 apparently have similar shapes, but the maximum yield of about 16 or 17 lbs is displaced from about 750° F at 900 psig to about 600° F at 300 psig. The 600 psig trend for xylenes is similar to that for 300 psig, with a maximum of 15 or 16 lbs at about 600° F. Apparently at the higher pressure of 900 psig the temperature must be increased about 150° F to obtain the same amount of degradation of the xylenes. Presumably the higher pressure inhibits the cracking of the xylenes.

At 300 and 600 psig the total aliphatics declined with increasing temperature, as might be expected on the assumption that the aliphatics in the tar would be increasingly cracked to gas with increasing temperature. However, as shown in Figure 7, at 900 psig the aliphatics rose from the value of about 5 lbs at 650° F, held in common with the 300 psig run at this temperature, to a value of about 7 lbs at 750° through 950° F, a 40 pct increase. About 2 to 5 lbs aliphatics was typical for the light oil from this same coal in ordinary low-temperature carbonizations (3, 4). Presumably at the higher pressure of 900 psig, cracking of the light oil boiling range aliphatics to gas was suppressed, whereas the higher molecular weight aliphatics in the tar were broken down to increase the yield of light oil aliphatics with increase in temperature. This was demonstrated by conducting urea extractions on the 900 psig oil products boiling above 200° C. The amounts of n-aliphatics decreased to the point that none could be extracted.

CONCLUSIONS

1. The optimum operating conditions for conversion of the combined tar vapors and liquid low-temperature tar immediately upon being produced from an hvab coal were a hydrogen pressure of 600 psig and a hydrodesulfurization catalyst temperature of 750° F.
2. Under these conditions about 100 lbs or 14 gallons of gasoline boiling range light oil could be obtained per ton of dry ash-free coal. Previous investigations indicate that this is probably a typical yield for low-pressure hydrogenation with fixed-bed carbonization of hvab coal. Yields would be higher with fluidized-bed or entrained-bed carbonization.
3. This colorless, sweet smelling, olefin-free product, which contained about 70 wt-pct BTX and little or no sulfur, nitrogen, and oxygen might be suitable for blending in the production of nonleaded gasoline.
4. The unusually low optimum hydrogen pressure of only 600 psig for this particular process would allow substantial reduction in plant cost compared with other processes in which pressures of 1500 psig, or higher, are required.

REFERENCES

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TABLE 1. - Operating conditions and material balances

Run no.	Bed temp., °F	Catalyst temp., °F	Hydrogen pressure, psig	Coal charged, g	Catalyst: coal ratio	Material balance on wt-pct coal as charged ^a			
						Char	Water	Total oils	Gas and loss
1	1,050	ND ^b	600	1,816	0.25	68.2	---	15.5	16.3
2	1,000	ND	300	1,816	0.25	71.2	8.8	5.6	14.4
3 ^c	1,000	ND	900	1,816	0.25	64.3	9.7	4.6	21.4
4 ^d	860	ND	300	1,816	0.25	82.7	3.9	2.6	10.8
5	920	ND	300	1,816	----e	75.6	4.3	8.8	11.3
6	810	ND	600	1,816	----e	79.6	3.8	5.5	11.0
7	930	ND	900	1,816	----e	74.6	4.6	5.1	15.7
8 ^f	830	ND	900	1,816	0.25	73.6	8.1	5.7	12.5
9	850	ND	300	1,816	0.10	73.2	6.6	6.4	13.8
10 ^g	720	ND	300	1,247.3	----e	89.1	2.1	3.0	5.9
11 ^h	960	ND	900	1,816	0.10	70.2	5.1	6.7	18.0
12	875	ND	0	1,816	0.10	72.1	5.3	12.7	10.0
13	865	750 ⁱ	0	1,816	0.10	67.9	4.6	9.2	18.3
14	890	755 ⁱ	300	1,816	0.10	69.1	6.7	8.3	16.0
15	980	745 ⁱ	900	1,816	0.10	69.3	6.2	5.8	18.5
16 ^j	925-940	745 ⁱ	300	1,816	0.10	77.1	8.1	6.3	8.5
17	850	725 ⁱ	900	1,816	0.10	71.5	8.4	6.6	13.5
18 ^j	885	645 ⁱ	300	1,816	0.10	78.1	7.7	7.5	6.7
19	950	640 ⁱ	900	1,823.6	0.10	76.8	7.2	6.1	9.9
20	950	745 ⁱ	600	1,816	0.10	69.2	8.3	7.6	14.8
21	950	650 ⁱ	600	1,816	0.10	75.8	7.6	6.1	10.4

a Determined by difference.

b Not determined; assumed to be about equal to bed temperature.

c Exothermic gasification; bed temperature over 1,200° F for 25 minutes.

d Blank run using nitrogen.

e Uncatalyzed.

f Rerun of No. 3.

g Rerun of char from No. 5.

h Possible leakage.

i Using separately heated catalyst reactor.

j Composite data of two runs.

TABLE 2. - Analysis of dewatered liquid products^a

Run no.	Distillation of total oil			GLC analysis of light oil			
	Total oil ^b	Light oil ^c	Heavy oil ^d	Residue ^e	Total aliphatics	Benzene	Toluene xylene
1	ND ^f	ND	ND	ND	ND	ND	ND
2	130	38	6	14	0.0	13.8	15.8
3	100	32	4	4	0.0	23.2	5.0
4	56	20	8	8	0.0	3.6	9.2
5	190	34	62	60	4.0	5.4	9.6
6	120	34	42	18	2.4	4.4	11.8
7	110	44	32	14	0.6	19.8	13.6
8	90	40	16	20	2.0	16.8	14.8
9	140	28	58	22	2.0	9.4	15.4
10	ND	ND	ND	ND	ND	ND	ND
11	144	40	66	66	6.8	14.8	16.8
12	276	28	62	116	6.2	0.8	7.4
13	200	10	66	64	1.4	1.4	3.6
14	180	56	74	28	4.2	16.8	19.2
15	128	72	12	26	4.0	23.6	24.8
16	146	66	16	32	0.4	13.2	29.0
17	156	84	0	50	7.0	12.6	30.4
18	172	66	34	36	5.6	5.6	17.6
19	140	66	30	14	9.4	5.0	20.6
20	176	96	36	16	6.4	29.0	28.6
21	144	76	38	10	8.4	5.8	16.0

a All data in lbs/ton dry ash-free coal.

b Includes oils trapped on silica gel but not recovered for distillation.

c lbp to 200° C.

d 200° to 400° C.

e > 400° C.

f Not determined.

TABLE 3. - Elemental analysis of light oils

Run No.	Weight-percent			
	C	H	N	S
1	Not determined			
2	91.9	8.0	0.08	0.1
3	91.9	8.0	0.08	0.08
4	89.3	8.8	0.2	0.3
5	87.7	9.8	0.3	0.4
6	87.6	9.3	0.2	0.3
7	89.0	8.9	0.4	0.2
8	90.7	8.9	0.05	0.1
9	90.8	9.3	0.02	0.03
10	Insufficient sample for analysis			
11	90.4	9.6	0.0	0.05
12	86.5	11.2	0.2	0.5
13	87.3	11.1	0.1	0.4
14	89.1	9.8	0.2	0.05
15	90.4	9.6	0.02	0.06
16	90.9	8.8	0.01	0.04
17	89.8	10.2	0.0	0.04
18	88.9	10.6	0.2	0.04
19	88.2	10.8	0.2	0.02
20	89.7	10.0	0.08	0.03
21	88.3	11.0	0.08	0.04

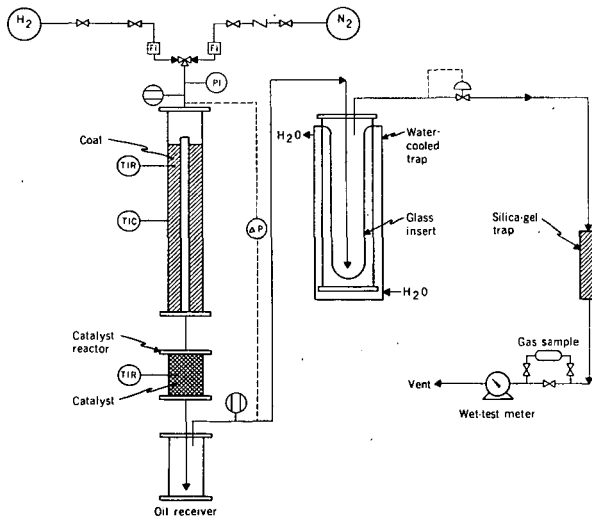


FIGURE 1. - Flow Plan of Hydrocarbonization Equipment for Catalytic Treatment of Tar Vapors and Liquids.

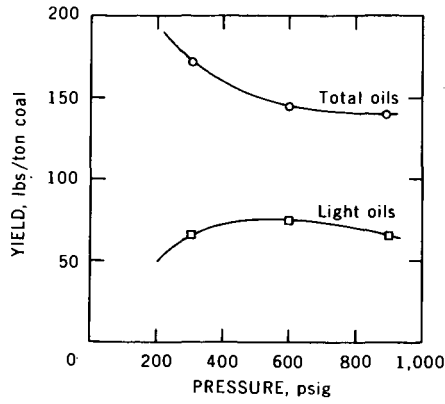


FIGURE 2. - Effect of Pressure on Yields of Total and Light Oils with 10 wt-pct Catalyst at 650° F.

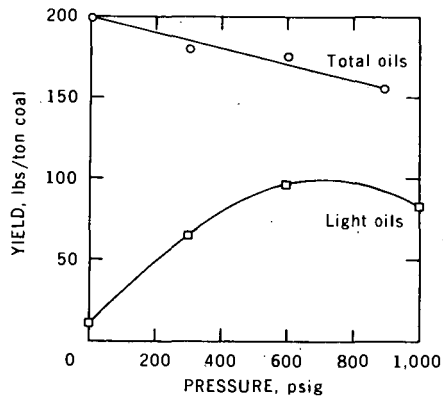


FIGURE 3. - Effect of Pressure on Yields of Total and Light Oils with 10 wt-pct Catalyst at 750° F.

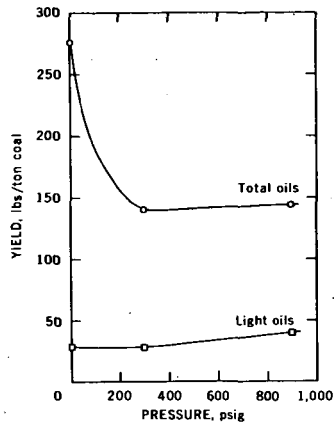


FIGURE 4. - Effect of Pressure on Yields of Total and Light Oils with 10 wt-pct Catalyst at 950° F.

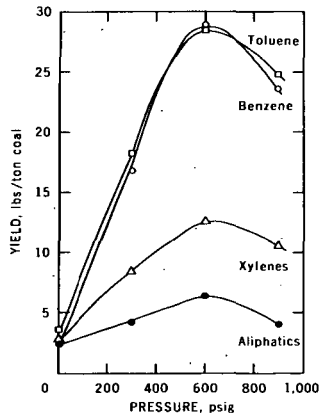


FIGURE 5. - Effect of Pressure on Yields of Major Light Oil Components with 10 wt-pct Catalyst at 750° F.

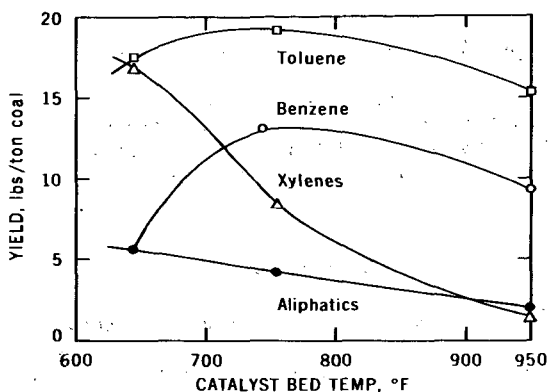


FIGURE 6. - Effect of Catalyst Bed Temperature on Yields of Major Light Oil Components at 300 psig.

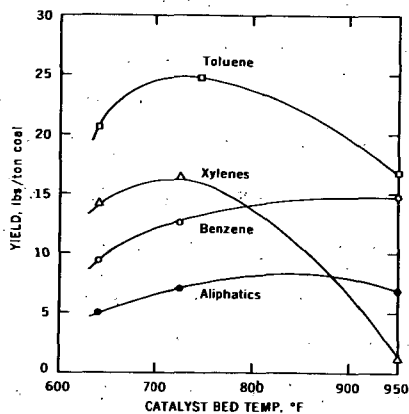


FIGURE 7. - Effect of Catalyst Bed Temperature on Yields of Major Light Oil Components at 900 psig.